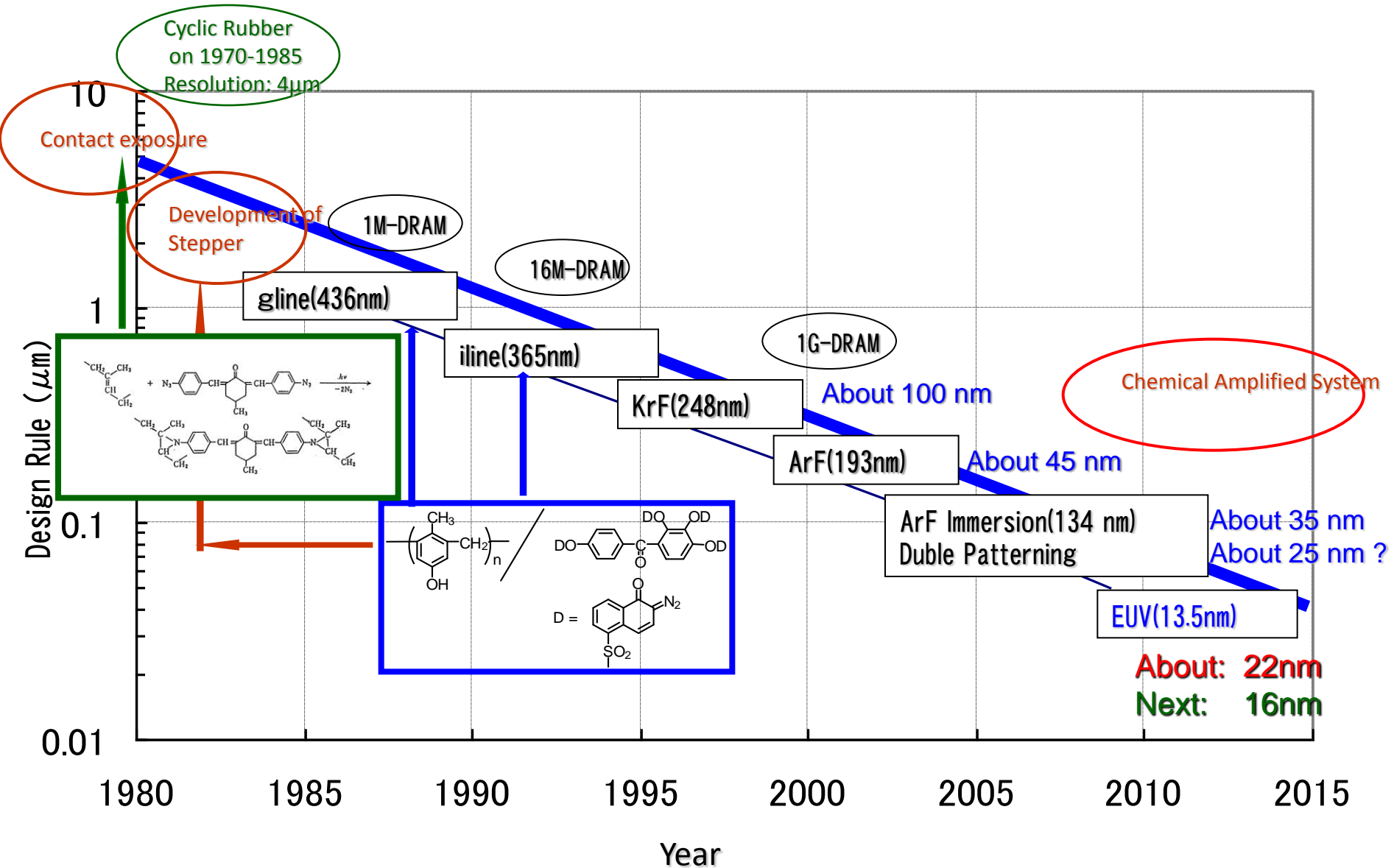


Development of Novel Molecular Resist Materials based on Ladder-Type Cyclic Oligomers for Extreme Ultraviolet Laser Exposure System

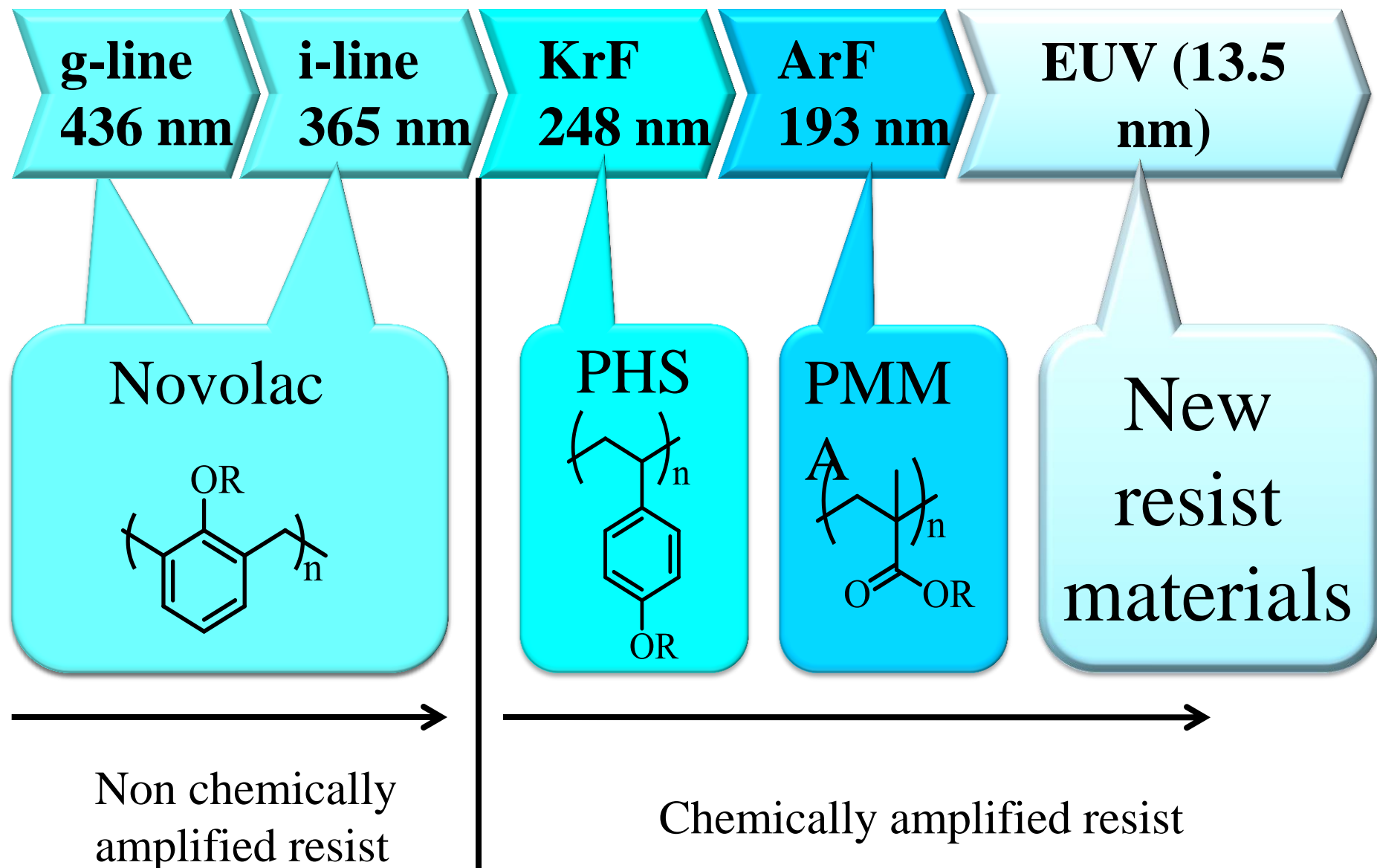
Hiroto Kudo* and Shuhei Matsubara

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35, Yamate-cho, Suita-shi, Osaka, 564-8680, Japan

Progress of Photo-lithography



Development of Lithography technology and resist materials

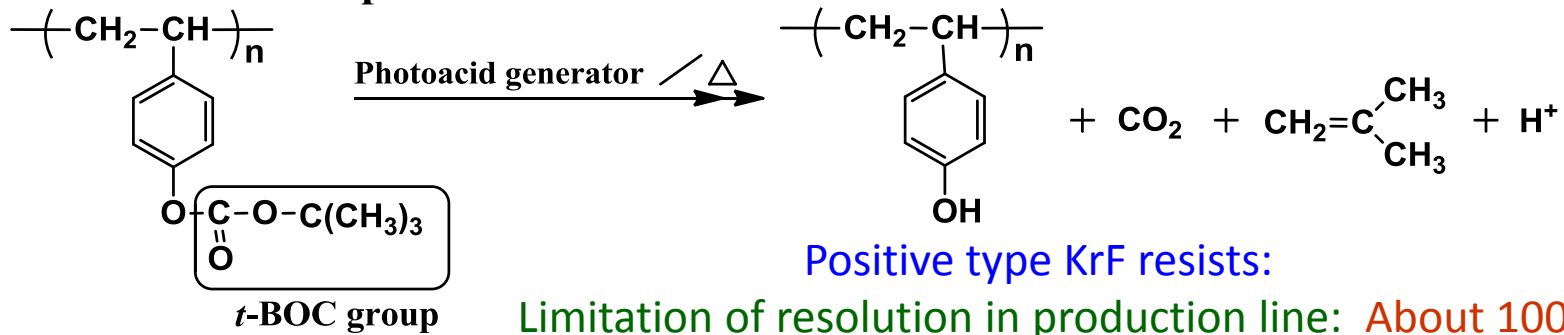


H. Ito, *Adv. Polym. Sci.*, **172**, 37 (2005).

H. Kinoshita, K. Kurihara, Y. Ishii, and Y. Torii, *J. Vac. Sci. Technol.*, **B7**, 1648

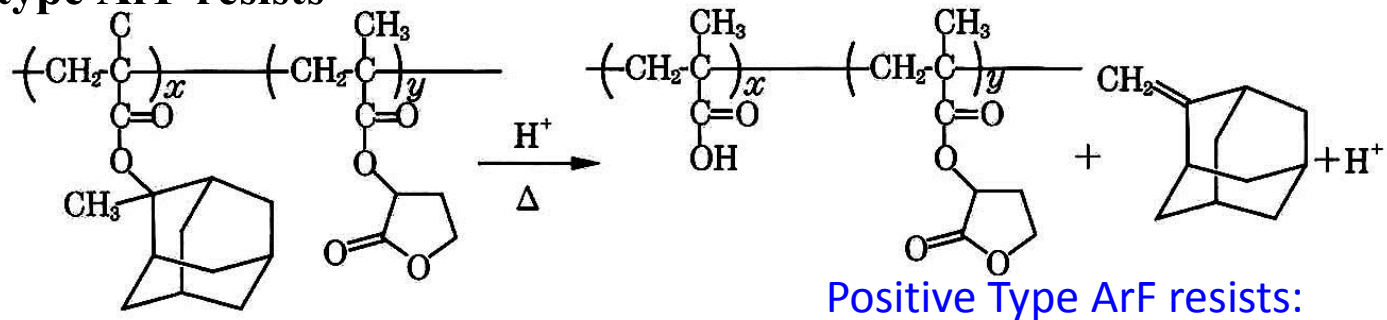
Typical Example of Chemical Amplified Resists

1. Poly(*p*-hydroxystyrene)s containing *t*-BOC group have been used as positive-type KrF resists for the production of semiconductor devices



1) C. G. Willson, H. Ito, J. M. J. Frechet, T. G. Tessier, F. M. Houlihan, *J. Electrochem. Soc.*, 133, 181(1986).

2. Copolymers containing both adamantane and lactone groups have been used as positive-type ArF resists



1) K. Nakano, K. Maeda, S. Iwasa, and E. Hasegawa, *Proc. SPIE*, 2438, 443 (1995).

2) E. Hasegawa Ed., *Organic Electronics*, p. 38 (2005).

New advanced technology and novel materials are required to achieve higher resolution

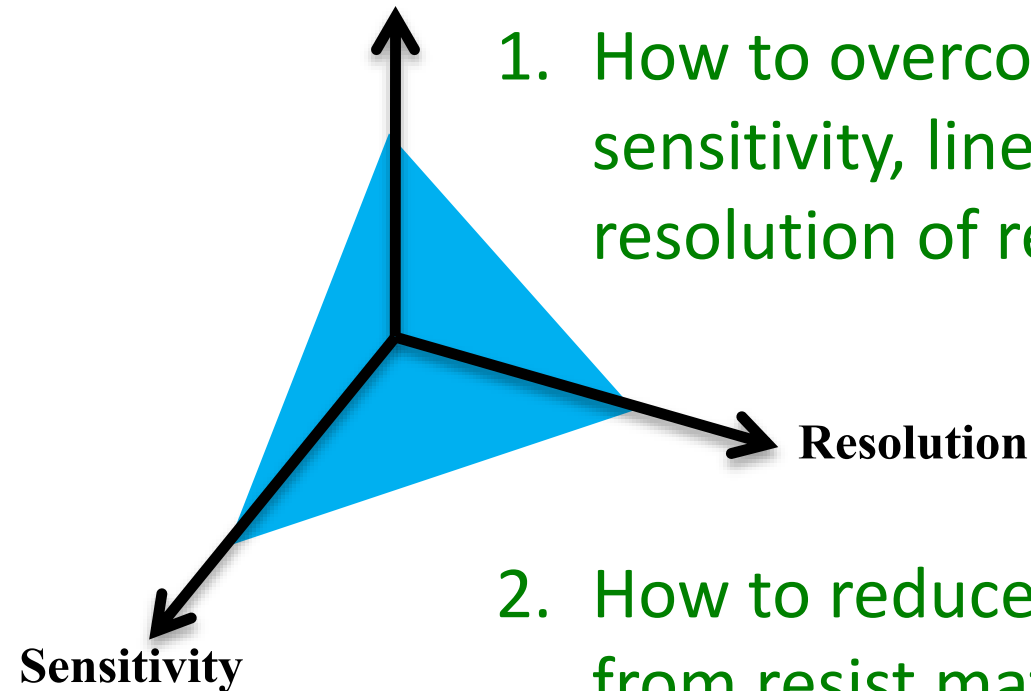
Latest New Technology:
EUV (13.5 nm) lithography
—Development of New EUV Resists—

Requirement of resist materials for EUV systems

Resolution of resist pattern	less than 20 nm
Sensitivity under EUV exposure	2~ 5 mJ/cm ²
LER of resist pattern	less than 1.5 nm

Other technical problem of EUV resist to achieve high resolution

Roughness: LER or LWR

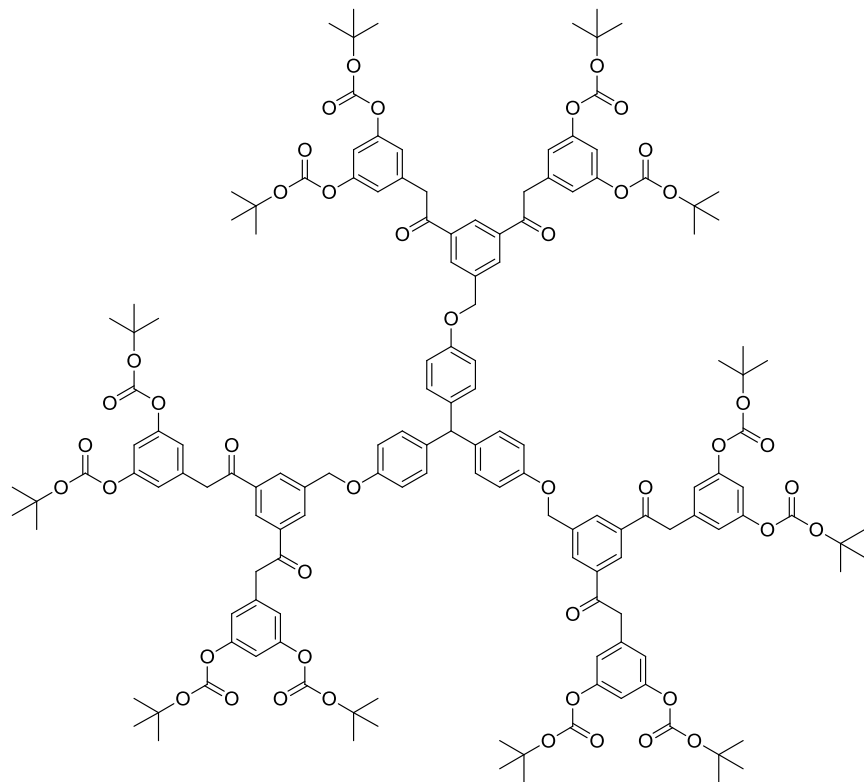


1. How to overcome Trade-off between sensitivity, line roughness, and resolution of resist materials.

2. How to reduce the produced out-gases from resist materials for prevention of mirrors in the tool by contaminate

Two different resist system can be considered

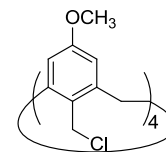
Molecular Glass Resist Materials



dendritic polymer resins

M. J. Frechet et al.

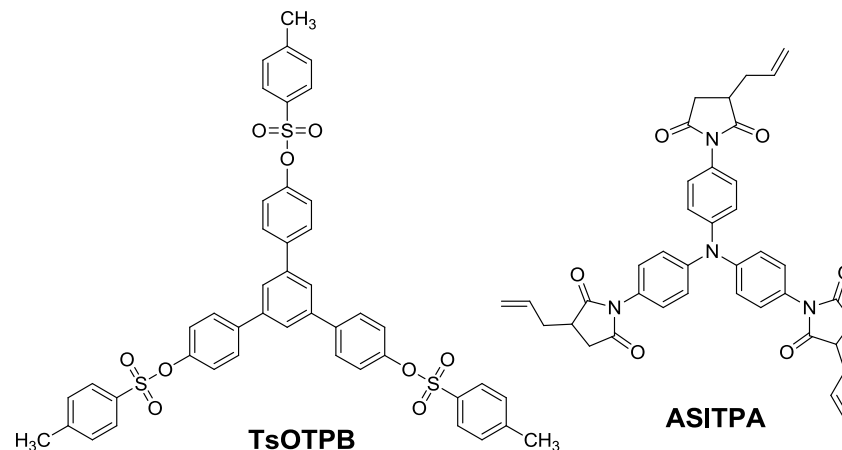
Acc. Chem. Res., 27, 151 (1994).



***p*-chloromethyl-methoxy-calix[4]arene**

E. Ochiai et al.

Appl. Phys. Lett., 68, 1297 (1996).

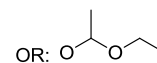
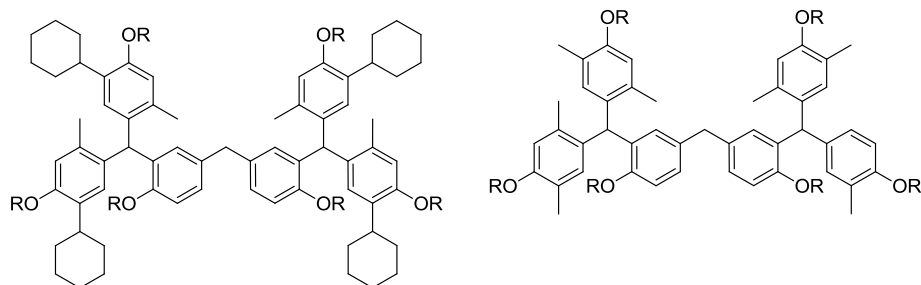


TsOTPB

ASITPA

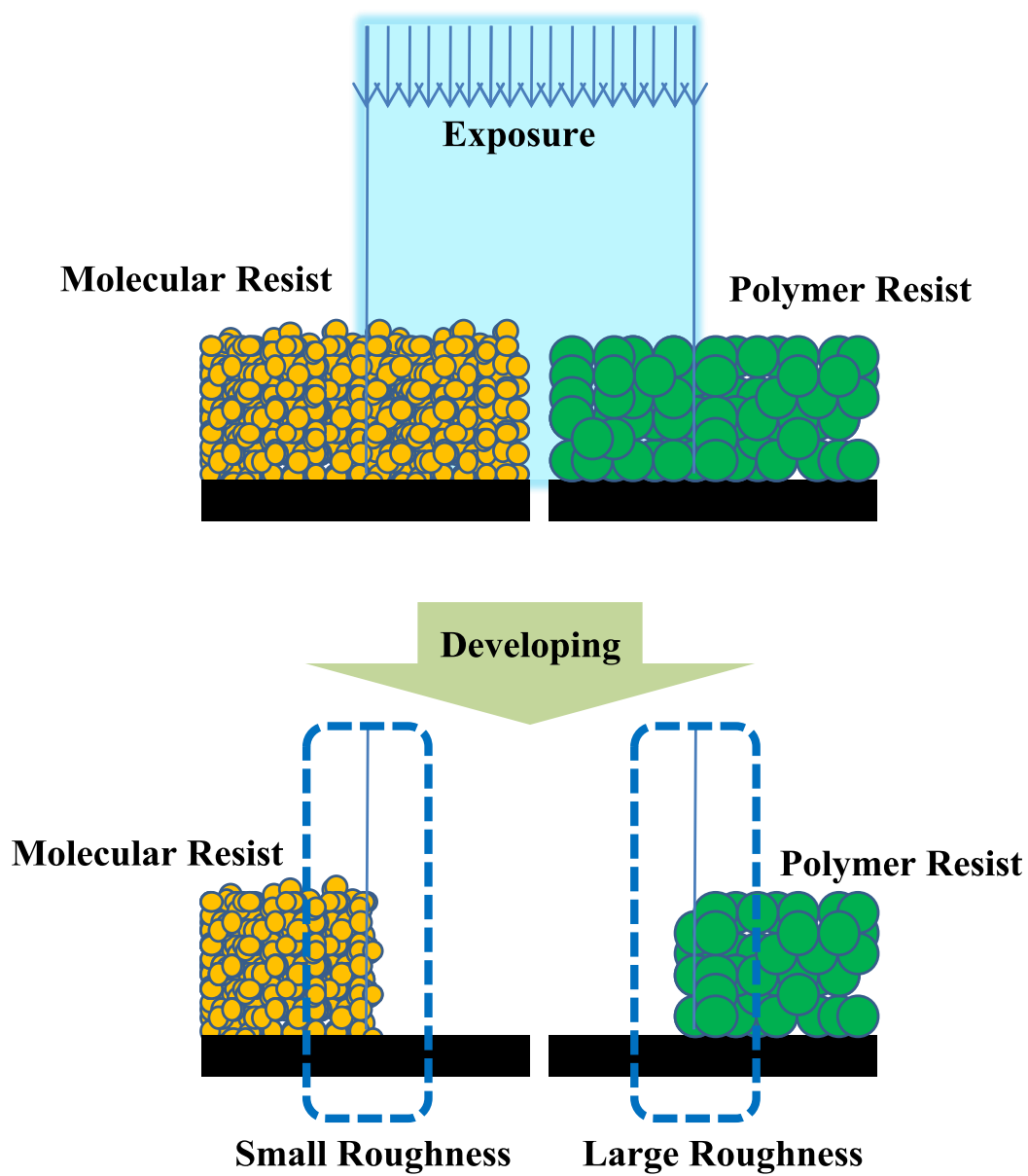
Shirota et al.

Chem. Lett., 33, 706 (2004).



T. Hirayama et al.

J. Appl. Phys., 44, 5484 (2005).



Imaging Design of Patterning Property of Polymer Resist and Molecular Resist

Photo-curing Reaction of Calixarene Derivative containing Methacryloyl Groups

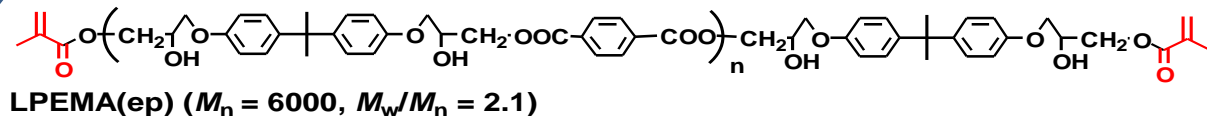
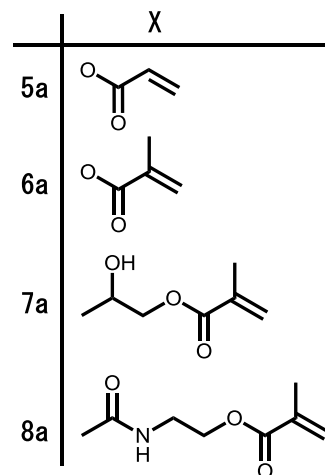
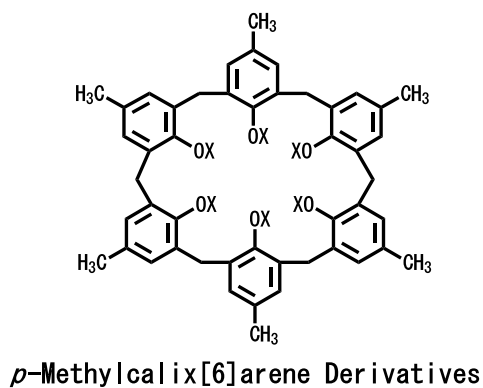
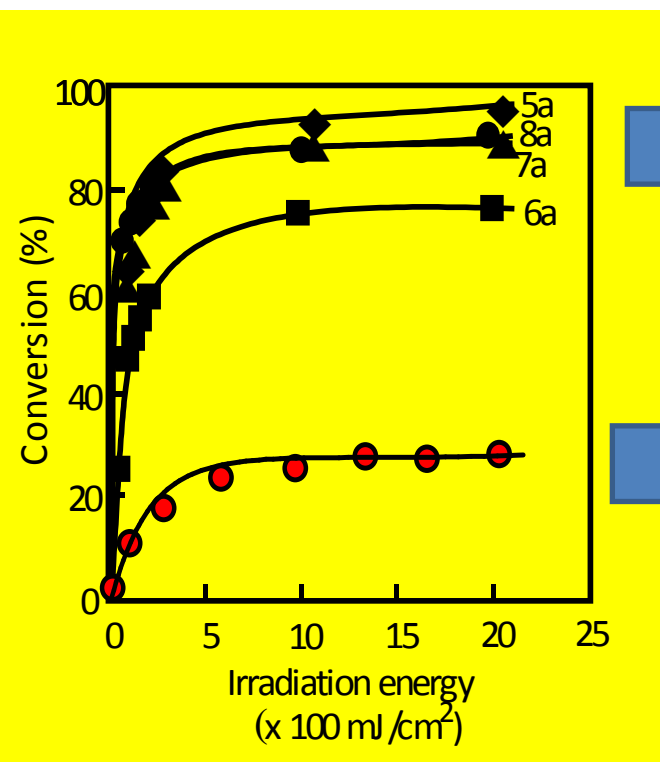
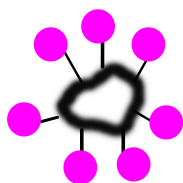


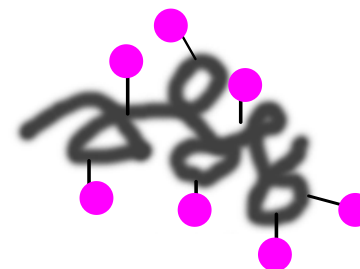
Photo Reactivity



Cyclic Oligomer



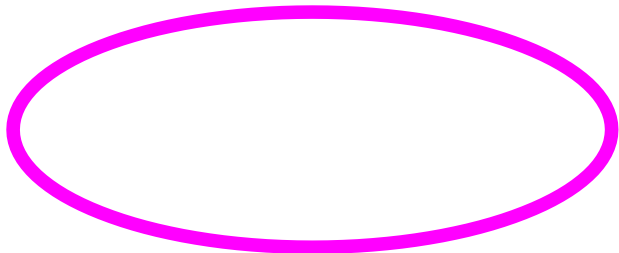
Polymer





Linear Oligomer

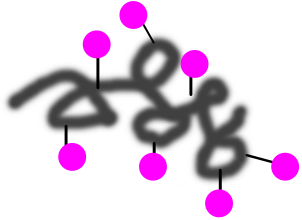
Glass Transition Temperature
Thermally Stability
Film-Forming Property



Cyclic Oligomer

Photo-functional Materials

Polymer



$M_w > 10,000$

Thermal
Stability



Film-forming
Property



Mechanical
Property



Photo
Reactivity



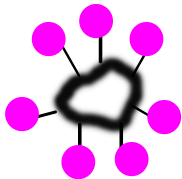
Oligomer



$M_w = 500 \sim 2,000$



Cyclic Oligomer

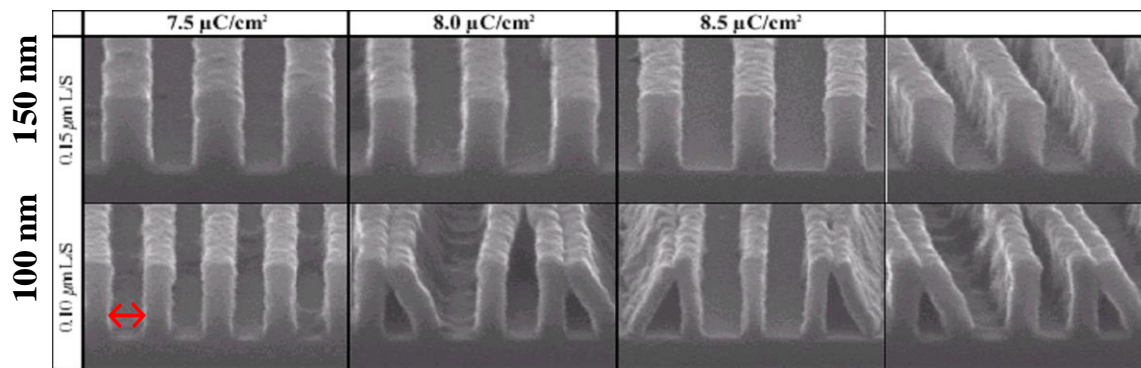
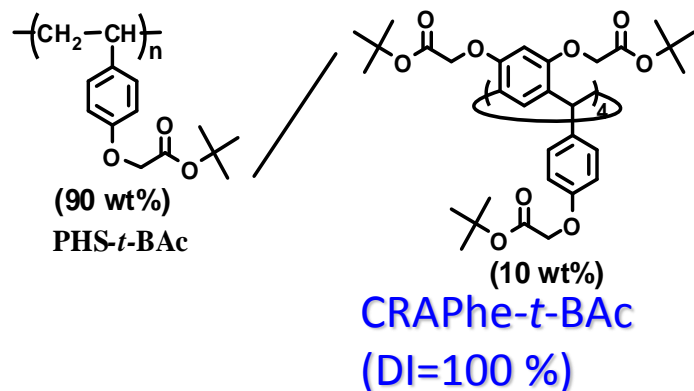


$M_w = 500 \sim 2,000$



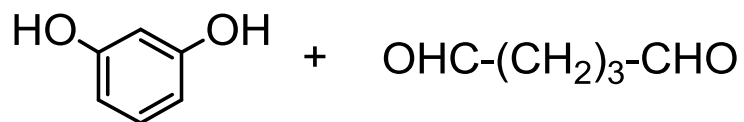
The other approach to achieve high resolution from CRA derivatives: *control of DI*

Patterning Properties by *EB* Lithography



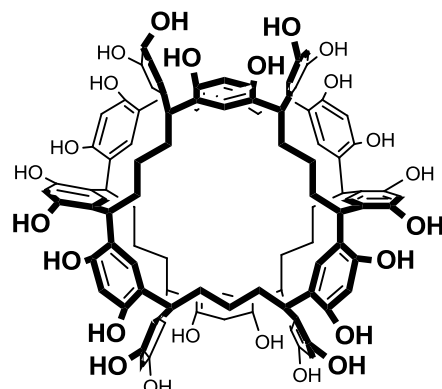
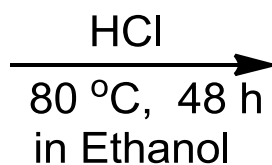
- 1) H. Kudo and T. Nishikubo et al., *Bull. Chem. Soc. Jpn.*, 77, 819 (2004).
- 2) T. Nishikubo, CSJ 88^t Spring Meeting, *Abstract CD-ROM*, 1C2-30 (2009).

The Synthesis of Noria

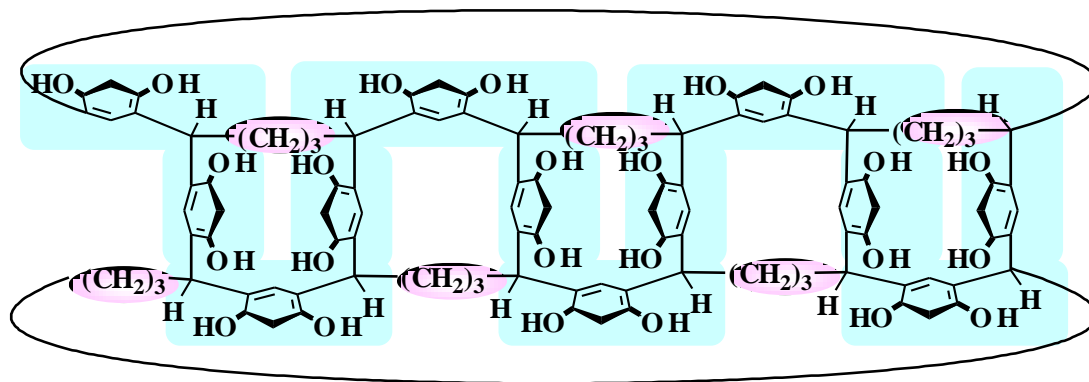
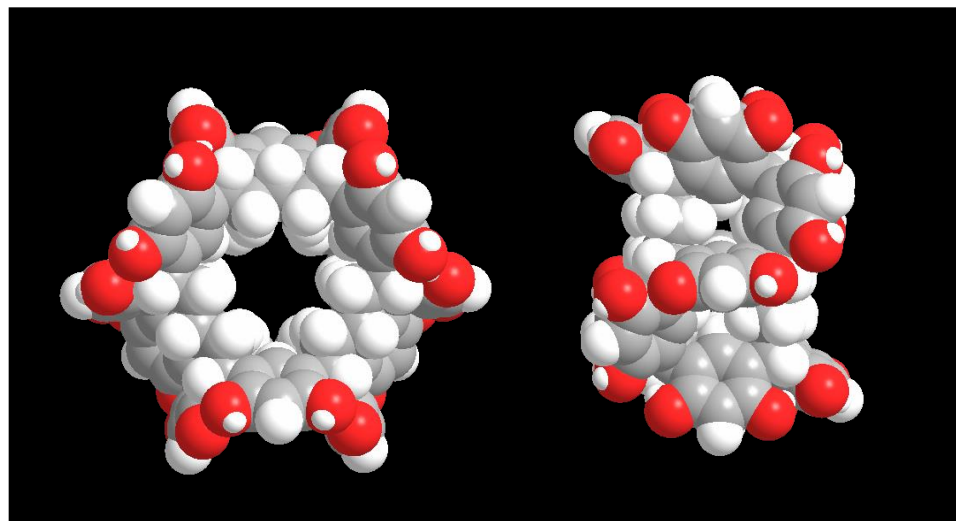


Resorcinol

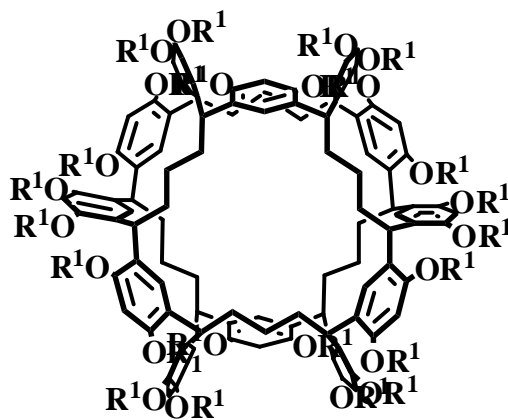
1,5-Pentanedial



Noria



Molecular resists based on Noria derivatives

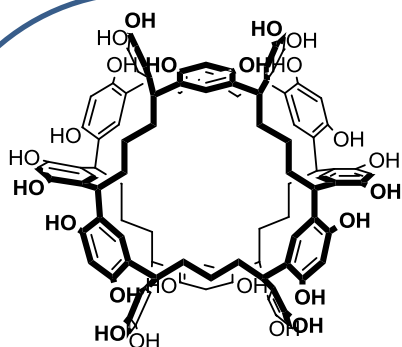


Noria derivative

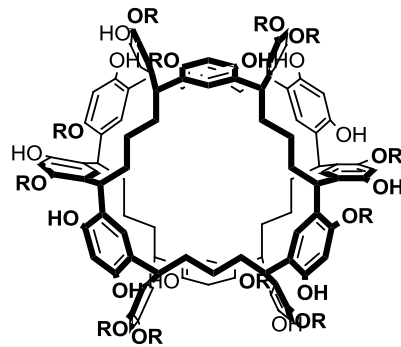
	noria-BOC	noria-BAc	noria-AD	noria-CHVE	noria-OX
OR ¹					
type	EB	EB	EUV	EUV	EUV
resolution	positive	positive	positive	positive	negative
	70 nm	50 nm	22 nm	35 nm	45 nm

Jpn. J. Appl. Phys. **50**, 121602-1-7 (2011). *J. Photopolym. Sci. Tech.*, **24**, 9 (2011). *Jpn. J. Appl. Phys.* **49**, 06GF06 1-6 (2010). *Journal of Materials Chemistry*, **20**, 4445 (2010). *J. Photopolym. Sci. Technol.* **23**, 657 (2010). *Journal of Materials Chemistry* **19**, 4622 (2009). *SPIE*, **6519**, 65194B (2007).

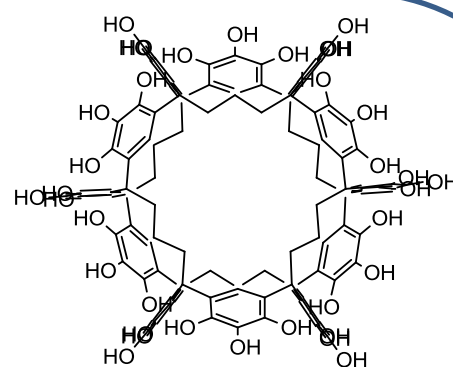
Certain Ladder-type Cyclic Oligomers



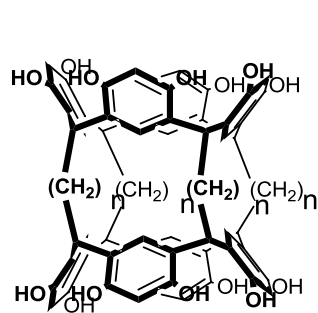
Noria



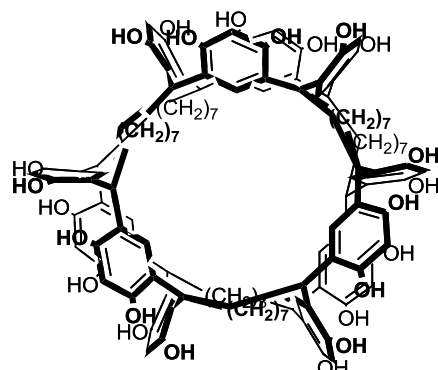
Noria-Alkoxy



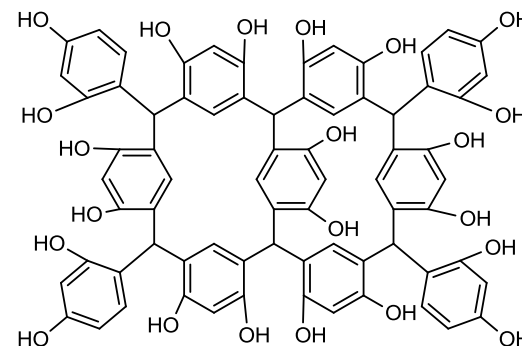
pyroNoria



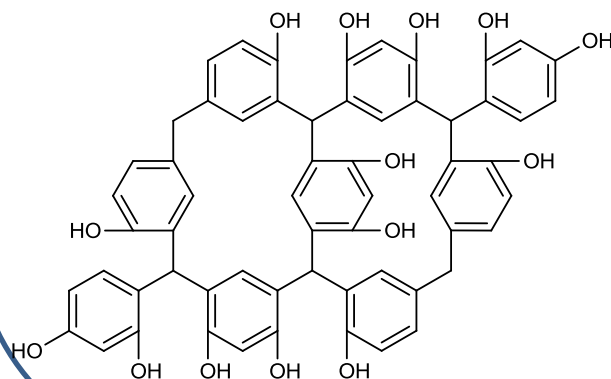
Calixarene-dimer



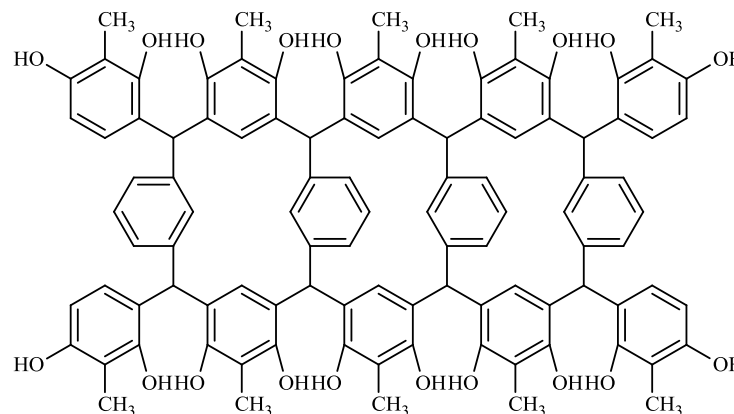
Calixarene-trimer



Double-Calixarene I



Double-Calixarene II



Triple-Calixarene

Molecular Sizes

Large

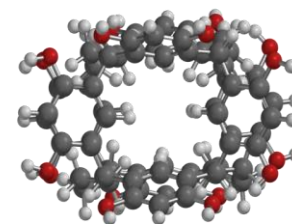
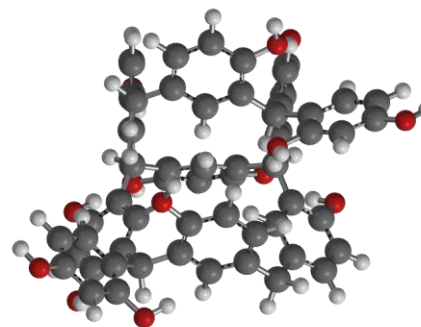
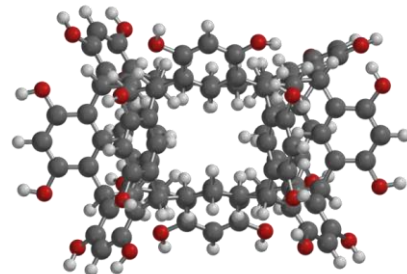
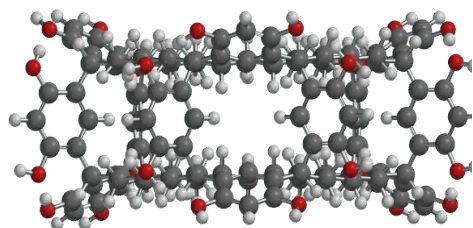
Small

CRA-Trimer

Noria

Double-ringed

CRA-Dimer



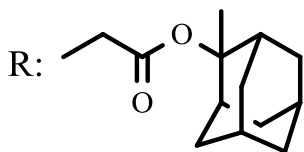
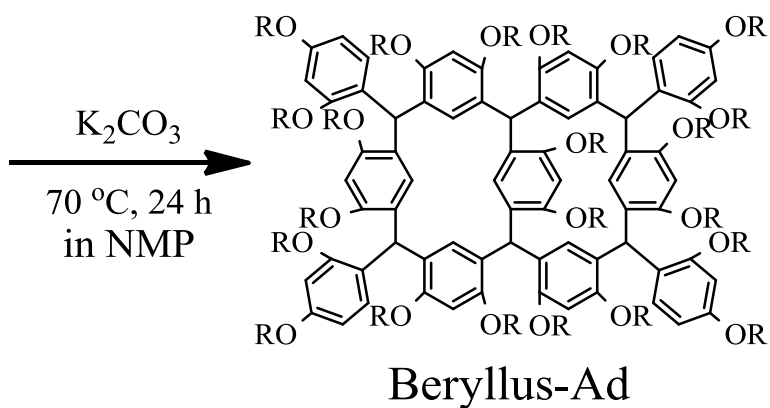
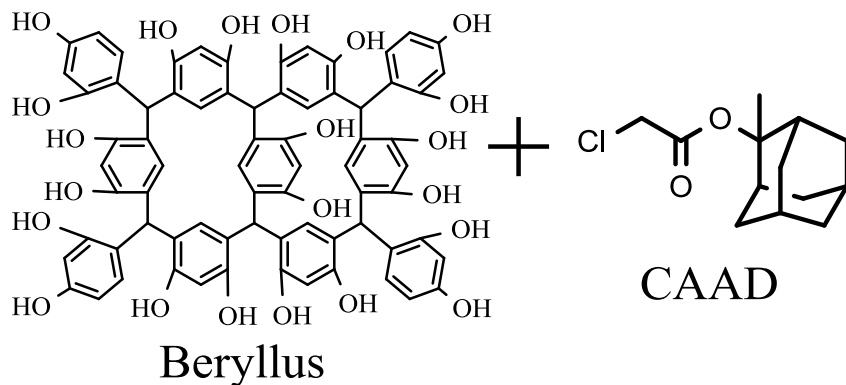
2.23 nm

1.8022 nm

1.5396 nm

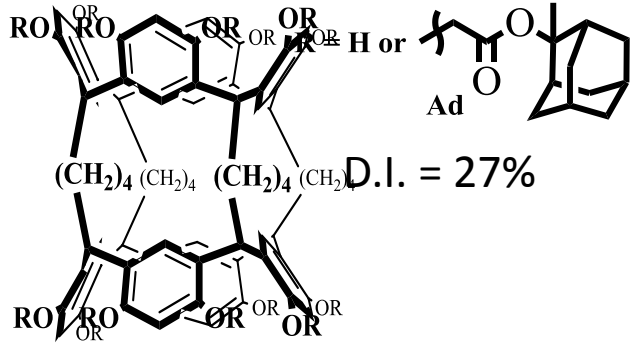
1.24 nm

Double-ringed arene derivatives with pendant adamantyl ester moieties



**EUV exposure
pattern could
not be obtained.**

Patterning property of the CRA-Dimer-Ad₂₇



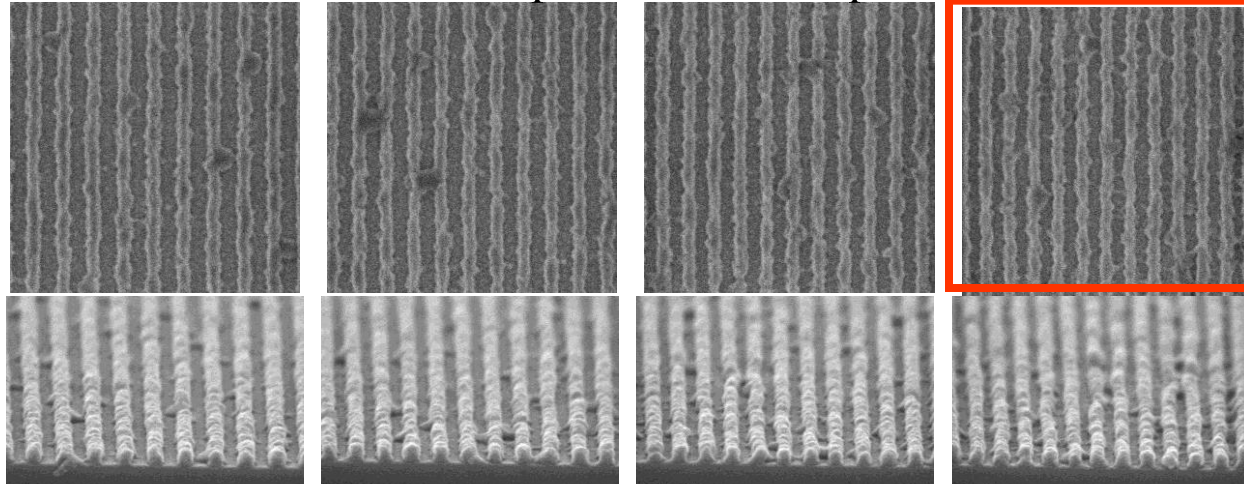
CRA-Dimer

35 nm-hp

32 nm-hp

30 nm-hp

28 nm-hp



Exposing

Sensitivity is not sufficient!

Resist : PAG (TFS-NF) :

Quenter (TOA) : 100 : 10 :

1.25 (wt%), 2.1wt%

PGMEA : Si wafer

Exposure:dose : 77mJ/cm²

PAB : 130 °C – 60 s,

PEB : 130 °C – 60 s

DEP : 2.38% TMAH 30s

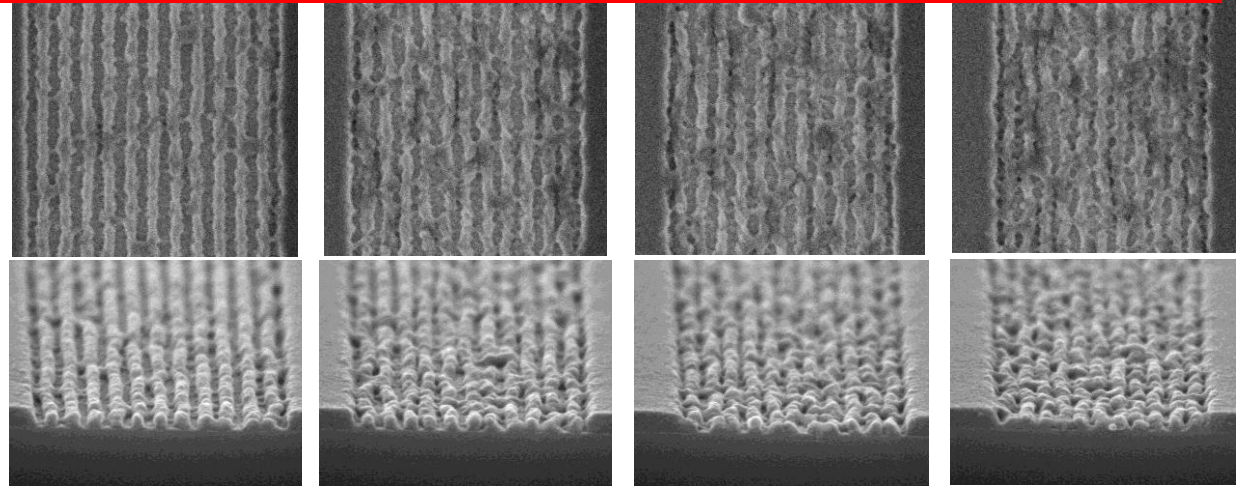


Figure. The obtained patterns in EUV expose system(dose : 77 mJ / cm²).

Molecular Sizes (*diameter*)

Large

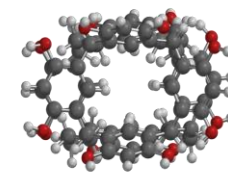
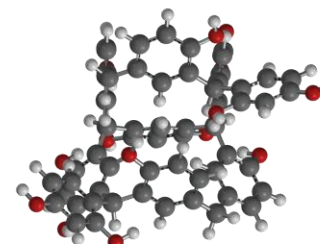
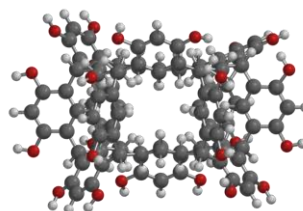
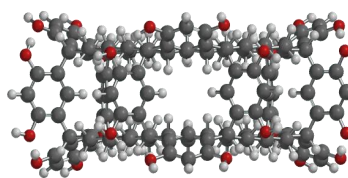
Small

CRA-Trimer

Noria

Double-ringed

CRA-Dimer



diameter

2.23 nm

1.8022 nm

1.5396 nm

1.24 nm

Exposure Dose (mJ)

?

14

X

77

Resolution (nm)

20

28

Molecular Sizes (*hole*)

Large

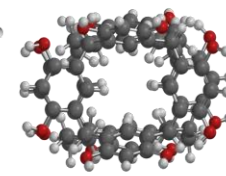
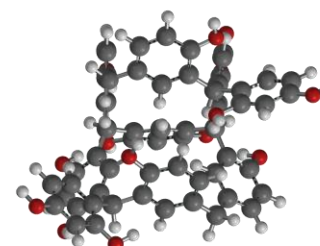
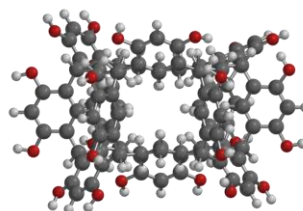
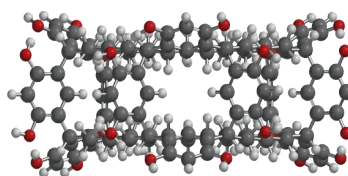
Small

CRA-Trimer

Noria

CRA-Dimer

Double-
ringed



hole

10 Å

3.4 Å

2 Å

1.3 Å

Exposure Dose (mJ)

?

14

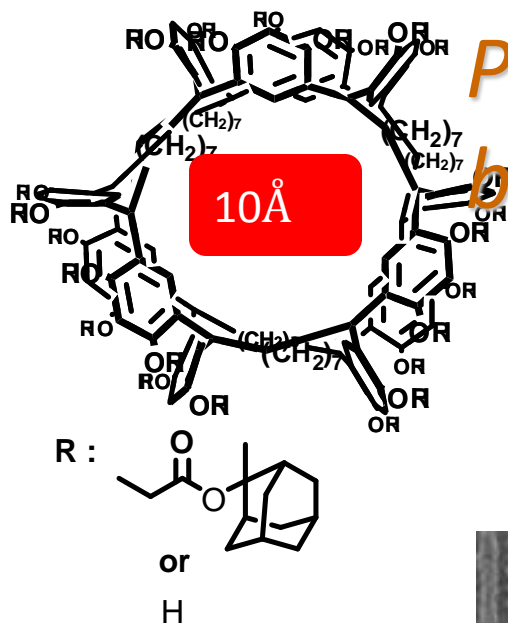
77



Resolution (nm)

20

28



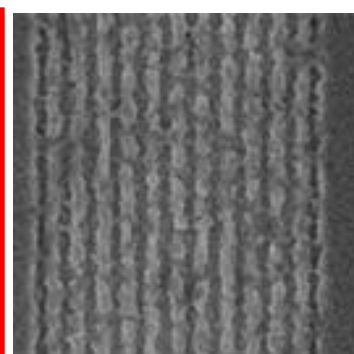
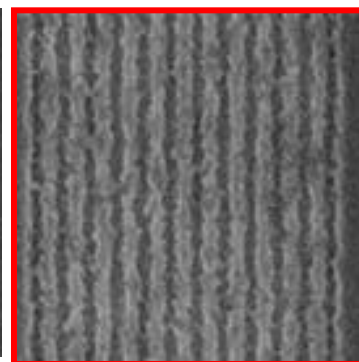
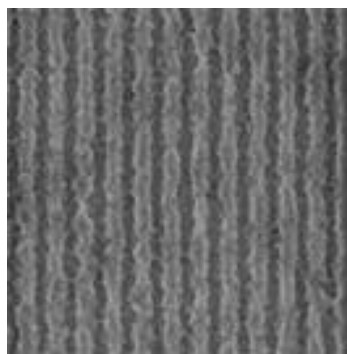
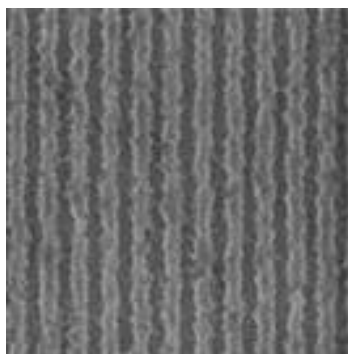
Patterning Properties of C7-Trimer-Ad₄₈ by EUVL (SEM Image)

30nm

28nm

26nm

24nm



C7-Trimer-MAd₄₈

TPS-NF/UL-M

Dose/CD/LWR
mJ/nm/nm

18/28.1/8.6

18/28.4/11.7

Process conditions:

PAB: 130°C-60s, PEB: 130°C-60s

DEP: 2.38%TMAH 30s

C7-Trimer MAd₄₈%

R:100/TPS-NF:10/TOA:1.25(wt ratio)

2.2wt% Diglyme solution:

Molecular Sizes (*diameter and hole*)

Large

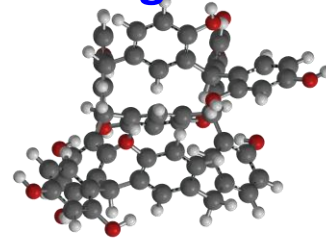
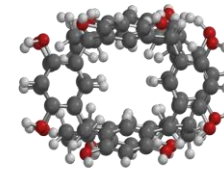
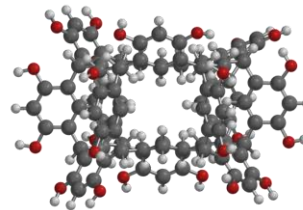
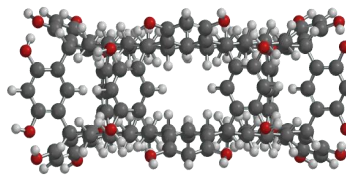
Small

CRA-Trimer

Noria

CRA-Dimer

Double-
ringed



diameter

2.23 nm

1.8022 nm

1.5396 nm

1.24 nm

hole

10 Å

3.4 Å

2 Å

1.3 Å

Exposure Dose (mJ)

18

14

77



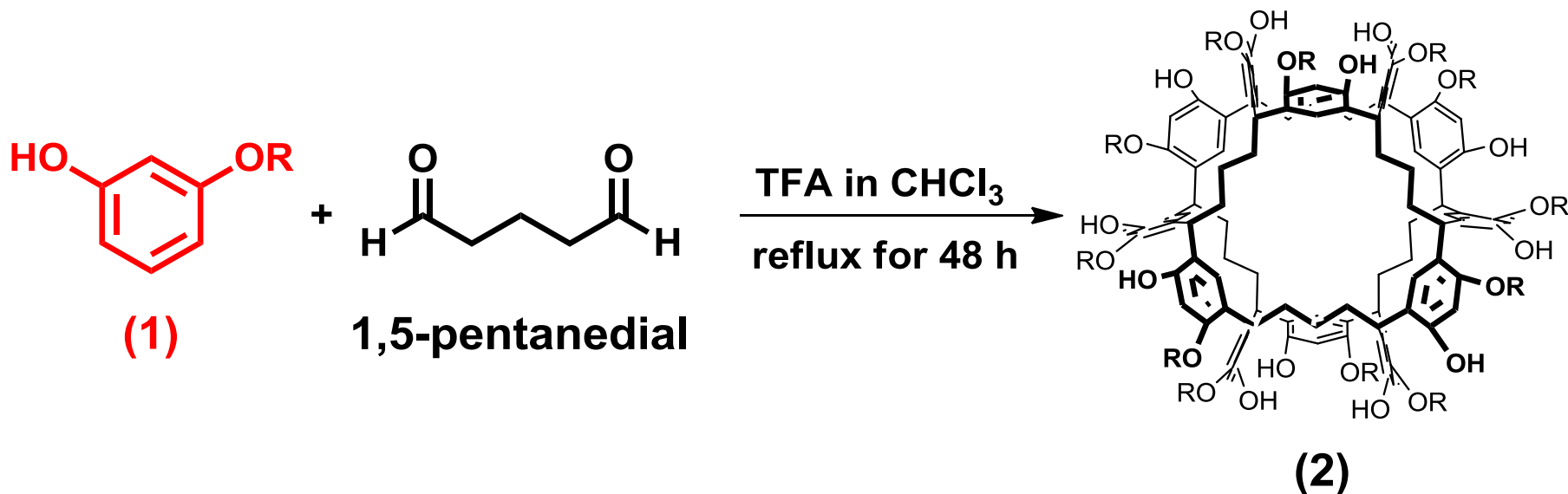
Resolution (nm)

24

20

28

Condensation reaction of 3-alkoxyphenol with 1,5-pentanedial



OR	1	2	Yield
OCH_3	3-methoxyphenol	noria-methoxy	87%
OC_2H_5	3-ethoxyphenol	noria-ethoxy	74%
OC_4H_9	3-butoxyphenol	noria-butoxy	52%

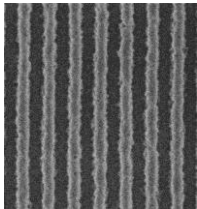
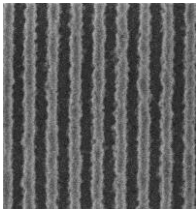
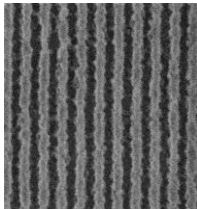
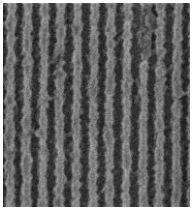
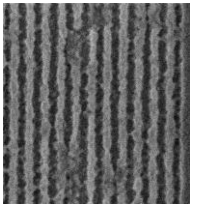
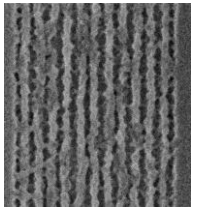
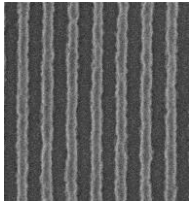
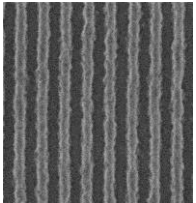
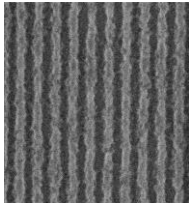
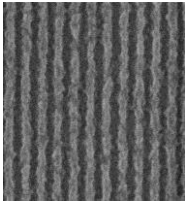
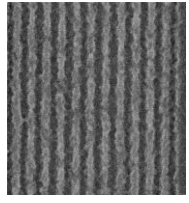
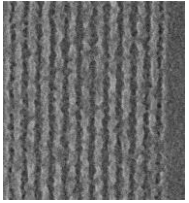
Solubility of noria, noria_{MP}, and noria_{MP}-AD_n

Solvent	noria	noria _{MP}	noria _{MP} -AD ₁₁ (DI = 11%)	noria _{MP} -AD _n (DI = 18 - 75%)
Water	-	-	-	-
DMSO	++	++	++	++
DMF	+-	++	++	++
Methanol	-	-	-	-
THF	-	++	++	++
Acetone	-	++	++	++
Ethyl lactate	-	+-		
Ethyl acetate	-	+-		
Ethyl ether	-	-		
Chloroform	-	++	++	++
PGMEA ^{a)}	+-	++	++	++
<i>n</i> -Hexane	-	-	-	-
Diglyme ^{b)}	-	++	++	++
PGME ^{c)}	+-	+-	+-	++
2.38wt% TMAH	++	++	+	-

**Good Solubility
And
Good Film-Forming Ability**

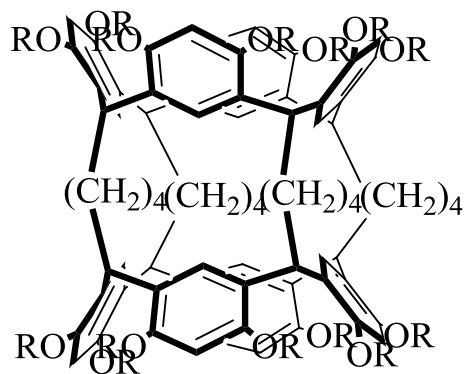
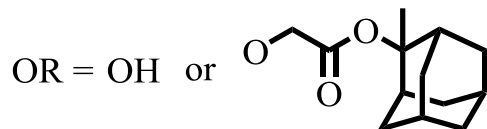
^{a)}PGMEA = propylene glycol monomethyl ether acetate, ^{b)}Diglyme = diethyleneglycol dimethyl ether, ^{c)}PGME = propylene glycol monomethyl ether, ++ ; Soluble at room temperature, + ; Soluble at heating, +- ; Partially soluble, - ; Insoluble

SEM image of noria_{MP}-AD_n.

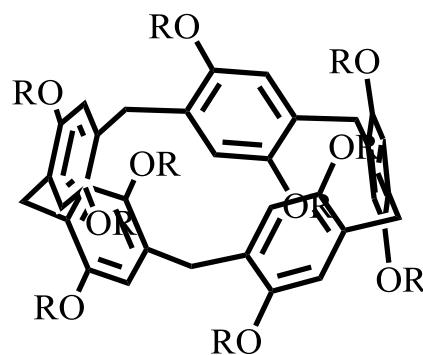
	(A)	(B)	(C)	(D)	(E)	(F)
Mask size L/S (nm)	50	Good Sensitivity				28
Noria _{MP} -AD ₁₈						
Dose (mJ/cm ²)	8.5	9.0	9.0	9.0	9.0	9.0
LER (nm)	6.1	7.7	10.5	- a)	- a)	- a)
Noria _{MP} -AD ₅₃						
Dose (mJ/cm ²)	10	10	10.8	10.8	10.8	10.8
LER (nm)	6.8	8.9	- a)	- a)	- a)	- a)

a)PGMEA = propylene glycol monomethyl ether acetate, b)Diglyme = diethyleneglycol dimethyl ether,
c)PGME = propylene glycol monomethyl ether, ++ ; Soluble at room temperature, + ; Soluble at heating, +- ; Partially soluble, - ; Insoluble

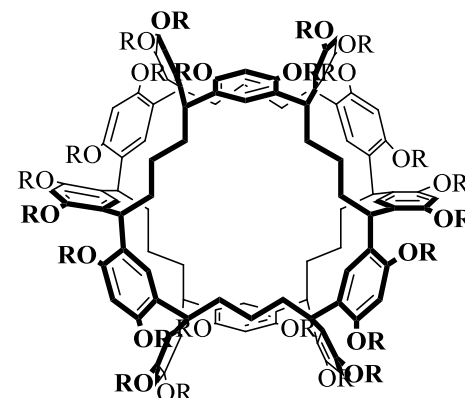
Evaluation condition of molecular resist



C₄-Dimer-Ad



Pillar[5]arene-Ad

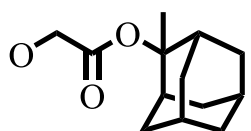
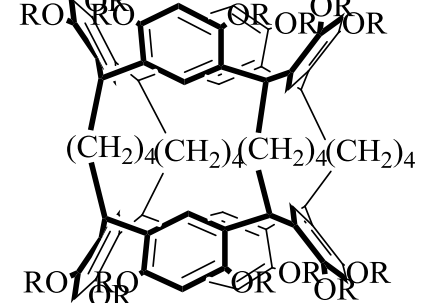
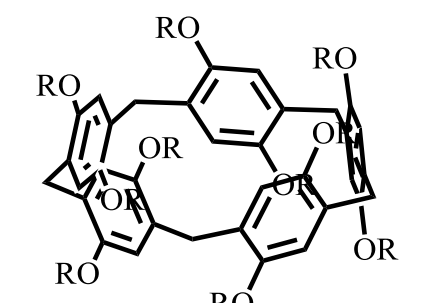
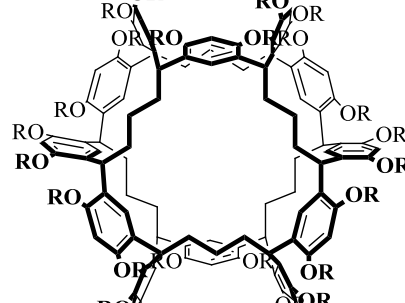
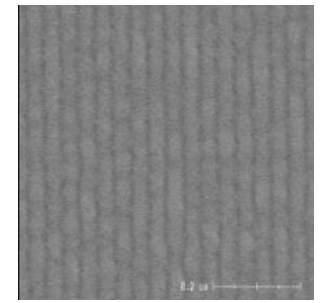
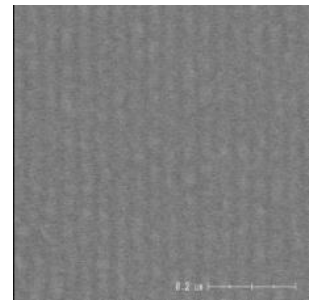
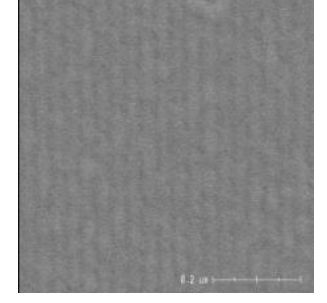
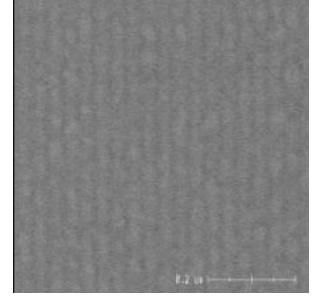
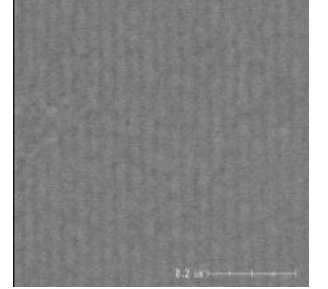


Noria-Ad

T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto
J. Am. Chem. Soc., 2008, 130 (15), pp 5022–5023

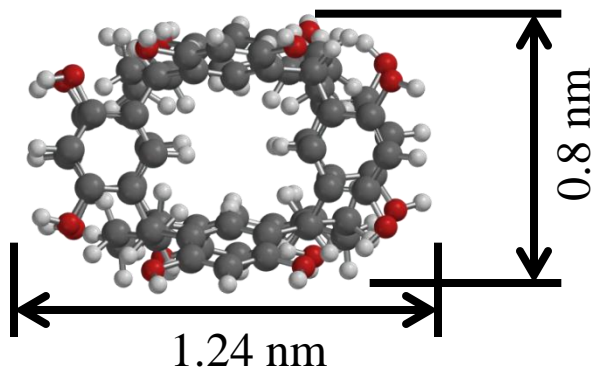
T. Ogoshi, T. Aoki, K. Kitajima, S. Fujinami, T. Yamagishi, and Y. Nakamoto
J. Org. Chem., 2011, 76 (1), pp 328–331

SEM images of obtained pattern

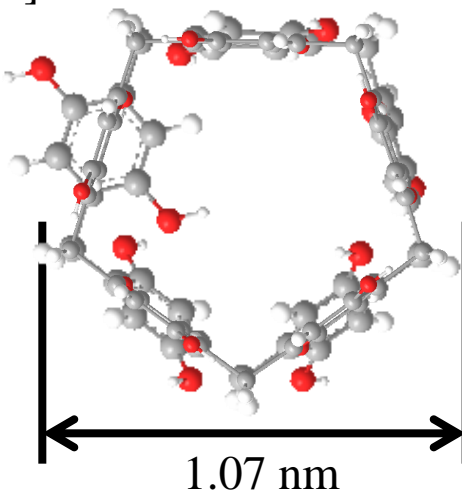
<p>OR = OH or </p>	 <p>C₄-Dimer-Ad</p>	 <p>Pillar[5]arene-Ad</p>	 <p>Noria-Ad</p>
20 nm L/S	No image		
17.5 nm L/S	No image		
15 nm L/S	No image	No image	

Sensitometric curves of C₄-Dimer-Ad and Pillar[5]arene-Ad

C₄-Dimer



Pillar[5]arene



Noria

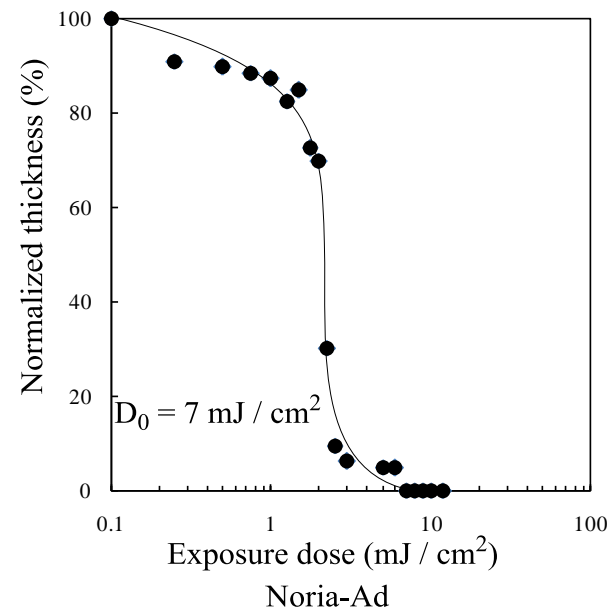
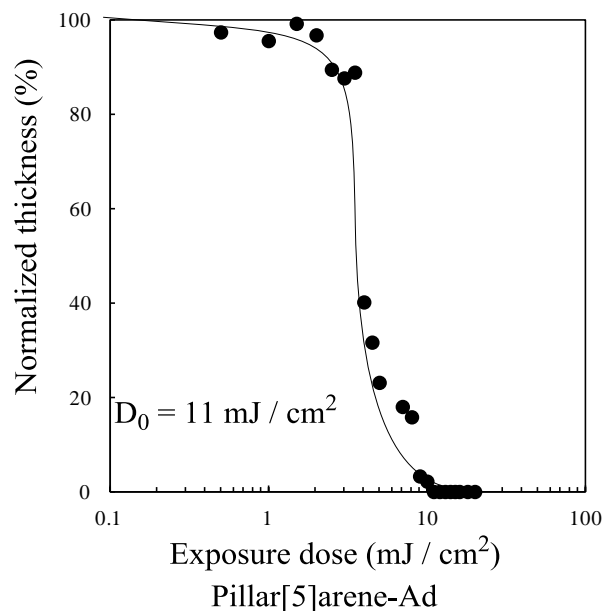
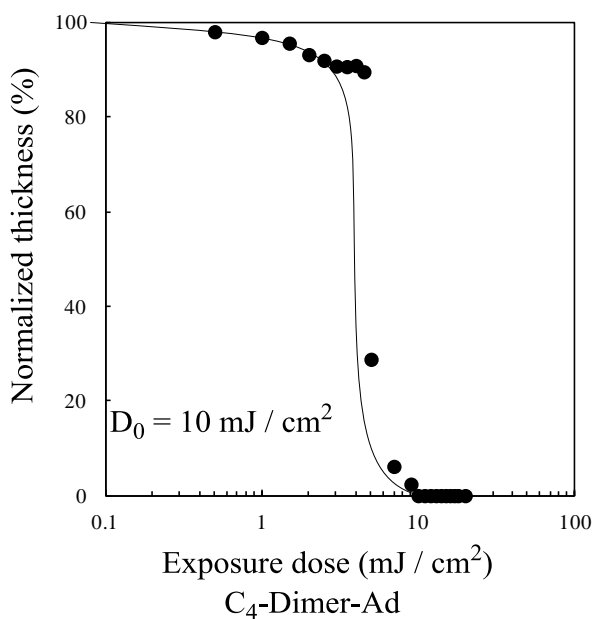
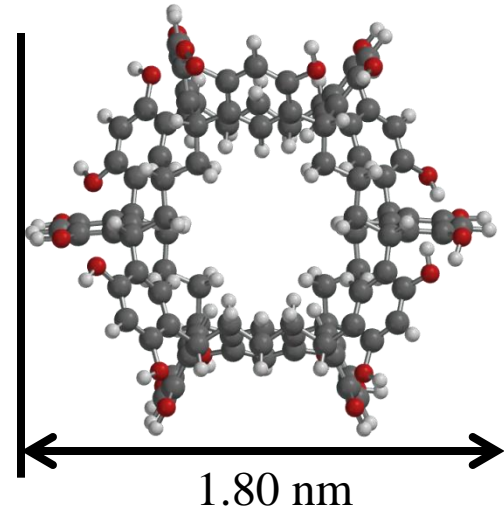
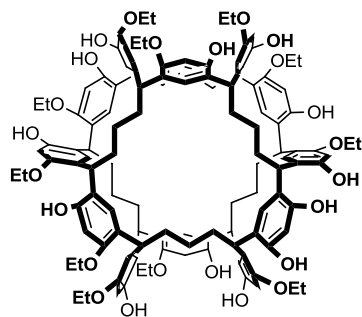


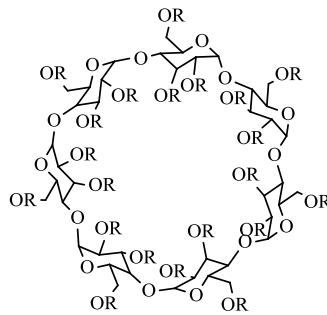
Figure. Sensitometric curve of C₄-Dimer-Ad (D.I. = 37%), Pillar[5]arene-Ad (D.I. = 35%) and Noria-Ad (D.I. = 40%).

1 mJ/cm²



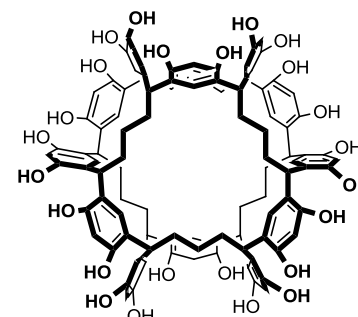
Noria-OEt

2 mJ/cm²



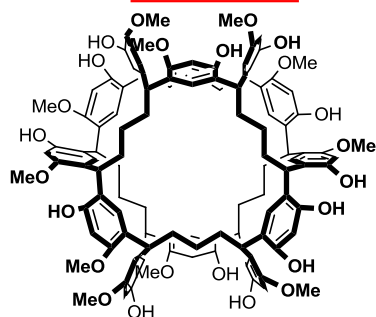
B-Cyclodextrin

7 mJ/cm²



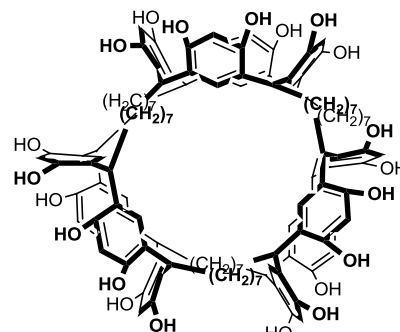
Noria

7 mJ/cm²



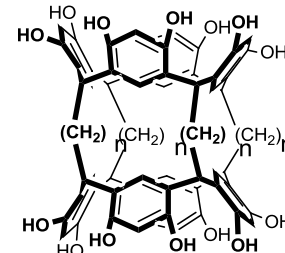
Noria-MeO

7 mJ/cm²



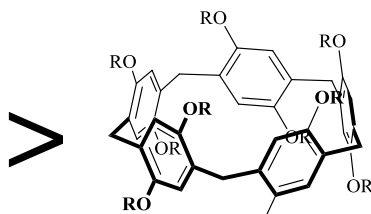
C₇-trimer

10 mJ/cm²



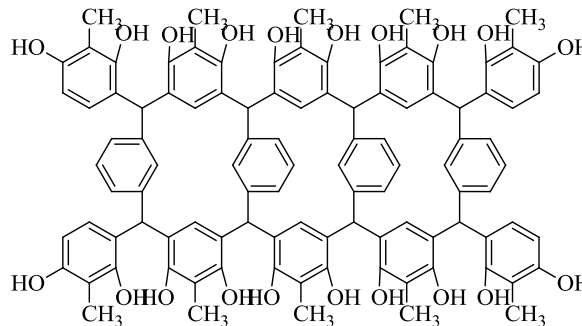
C₄-dimer

11 mJ/cm²



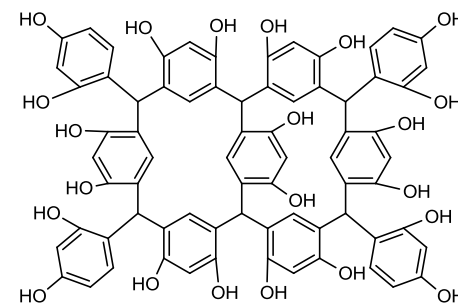
Pillar[5]arene

22 mJ/cm²



TCRA

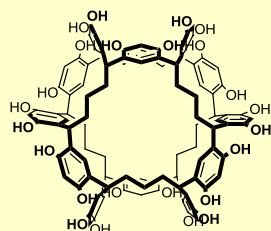
40 mJ/cm²



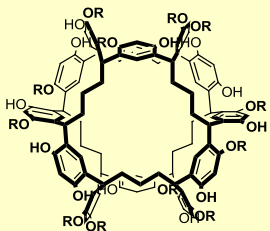
DCRA

Summary

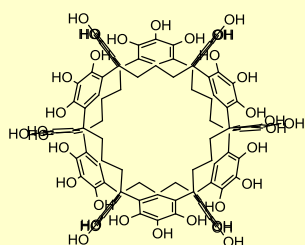
Next Generation EUV Resist Material



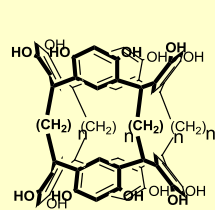
Noria



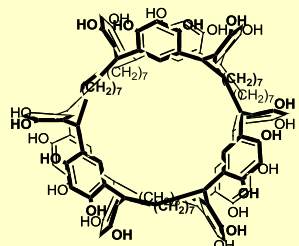
Noria-Alkoxy



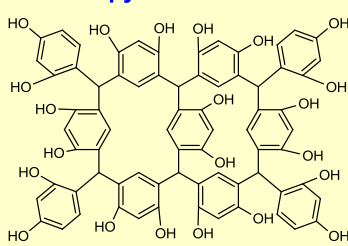
pyroNoria



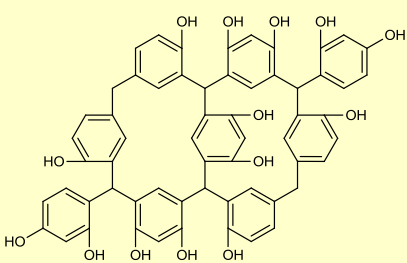
Calixarene-dimer



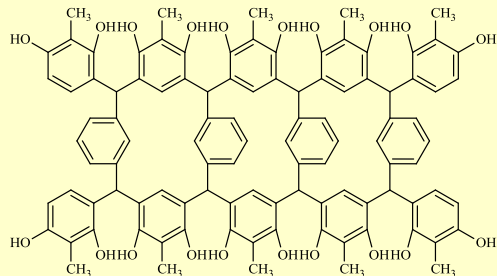
Calixarene-trimer



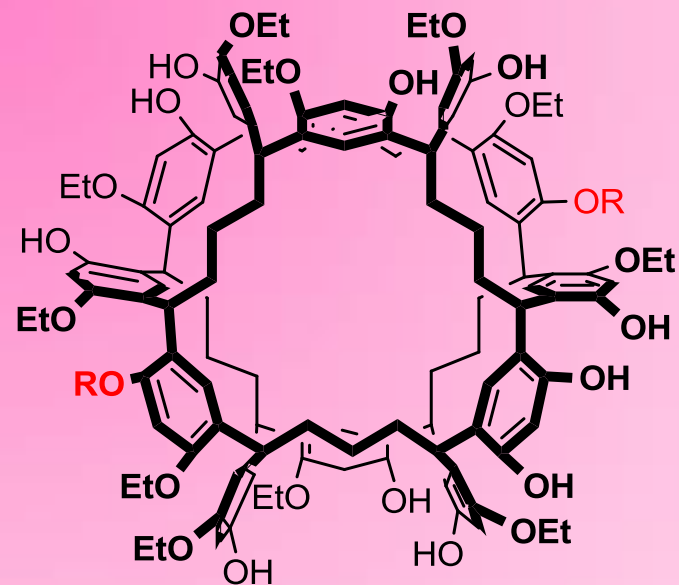
Double-Calixarene I



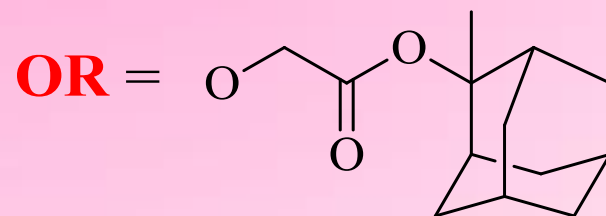
Double-Calixarene II



Triple-Calixarene



Noria-OEt



Excellent Sensitivity

Acknowledgement



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- Grant-in-Aid for Scientific Research in Japan (No. 18681015) from the Ministry of Education, Culture, Sports, Science, and Technology .
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The Institute of Scientific and Industrial Research, Osaka Univ.



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兵庫県立大学 UNIVERSITY OF HYOGO



**Prof. Takahiro
Kozawa**



**Assistant. Prof.
Hiroki Yamamoto**



**Prof. Hiroo
Kinoshita**



**Associate Prof.
Takeo Watanabe**